# Sub Second Liquid Transient ATR FT-IR Micro Flowcell for In-situ Analysis of Sorption Phenomena and Surface Kinetics

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Introduction

In kinetic measurements of catalysis, steady state experiments are the norm. However, a lot more information can be obtained from transient experiments where the catalyst is subjected to changing conditions and the response is followed in time. Transient experiments (e.g. TAP) [1] have been extensively performed for gas-phase catalysis, where low pressures and end of pipe analysis provide useful information on sorption phenomena and reaction mechanism. In liquid phase catalysis, the situation is further complicated because a step change in concentration is blurred by axial dispersion along the length and slow diffusion across the width of the channel. Currently liquid phase transients take longer than many surface dynamics to complete, making quantification near impossible. The objective of this work is to develop a device that allows transient analysis of surface chemistry of real catalysts in the liquid phase for processes that occur at the second scale. In order to obtain operando chemical information, we have chosen Attenuated Total Reflection (ATR) FT-IR spectroscopy [2]. This technique allows IR measurements to be performed on powder and liquids outside the crystal, showing both bulk and adsorbed species.
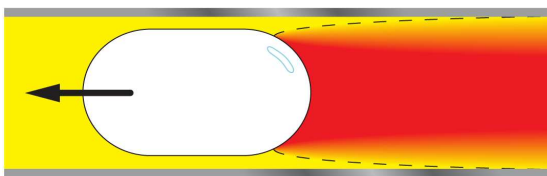
Figure 1. The old liquid bulk in the channel is pushed out by the gas slug, leaving a thin film layer near the channel wall. The gas slug is pushed out by the replacing liquid, which diffuses across the film layer.

The problem of shallow gradients is addressed using segmented flow (see Figure 1), by the introduction of an immiscible phase that separates the starting and final conditions. Segmented flow has a double function – it reduces both axial dispersion (mixing along the length of the reactor) and reduces the diffusional boundary near the wall, allowing for faster diffusion along the width of the channel. Available literature [3] allows prediction of the diffusional boundary. To obtain the 1 second switch time outlined in our objective, channel height must be on the order of 100 micron.

Materials and Methods

Microfabrication techniques were used to produce a flowcell with a channel with a cross-section of 0.1 by 1 mm. Measurements were performed on a modified Horizon ATR accessory (Harrick). Adsorption desorption measurements were performed for cyclohexanone in cyclohexane on titania, relevant for the selective photo oxidation of cyclohexane [4]. Deconvolution of IR absorption bands was performed using a custom routine in MATLAB.

Results and Discussion

When using segmented switching over an uncoated channel, a characteristic time of switching of 0.6 s is obtained (Figure 2). When a titania coating is introduced in the micro flowcell, switch time increases to 3.3 seconds (see inset Figure 3). Steady state adsorption behaviour of cyclohexanone in cyclohexane on titania was determined to be of the Langmuir type, with an overall adsorption constant $K=26\pm5$ m^3/mol. The desorption behaviour of cyclohexanone in cyclohexane over titania has a characteristic desorption time that is shorter than 3.3 seconds (Figure 3).
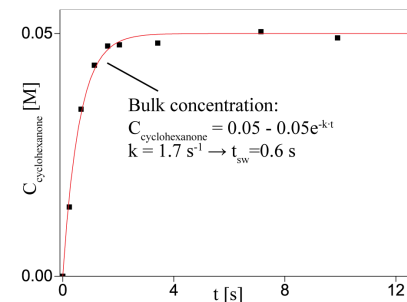
Figure 2. The concentration of cyclohexanone in cyclohexane during a segmented switch from 0 to 0.05 M cyclohexanone in an empty channel

Significance

The ATR microreactor allows the analysis of adsorption of liquid phase components on solid catalyst systems, and promises the possibility of operando studies on liquid phase heterogeneous catalysis. We have shown that sklow desorption of cyclohexanone is not the cause of deactivation in selective photo oxidation of cyclohexane.
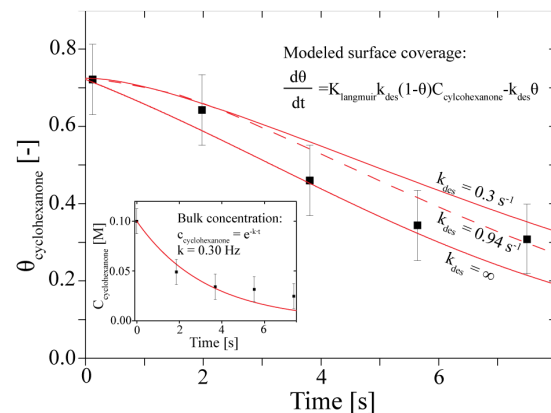
Figure 3. The cyclohexanone coverage in time is shown during desorption of cylohexanone in cyclohexane from titania. The bulk concentration of cyclohexanone is shown in the inset.

References

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